Analysis of ion-beam induced degradation of poly(vinylidene fluoride) and post-irradiation treatment for efficient track etching

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Ion-track membranes of poly(vinylidene fluoride) (PVDF), a type of fluoropolymer, could find wide applications due to its superior chemical and mechanical properties. In order to produce track-etched pores in PVDF films, a highly-concentrated alkaline solution with a strong oxidizing agent (e.g., $KMnO_4$) has mostly been used at a high temperature. Yet this provides irreversible chemical damage over the entire film including the non-irradiated part [1]. Thus, we have developed much milder etching conditions without any oxidant additives in the alkaline etching solution [2]. The goal of this work is to investigate the effect of post-irradiation treatment to pursue the possibility of accelerating the track etching rate. The discussion is given to this based on the detailed chemistry of heavy-ion-induced degradation, which was analyzed at the M-branch.

Commercially-available 25-μm thick PVDF films were irradiated at room temperature with 450-MeV ^{129}Xe ions at the TIARA cyclotron of JAEA, and with 2.2-GeV ^{197}Au ions at the UNILAC. The irradiation at UNILAC was performed in the multi-purpose chamber of the M3 beamline equipped with a Fourier-transform infrared (FT-IR) transmission spectrometer and a quadrupole mass. analyzer. The FT-IR spectra and the residual gas data were recorded in-situ as a function of fluence up to 6×10^{11} ions/cm^2. For the track-etching experiments, the irradiation at TIARA was performed at a lower fluence of 3×10^7 ions/cm^2. The irradiated film was etched in a 9 mol/dm^3 aqueous potassium hydroxide (KOH) solution at 80˚C. The track etch rate was determined via measuring the breakthrough time (T_B) in a conductometric etching cell.

The FT-IR analyses undoubtedly confirm that the irradiation efficiently produces C=C double bonds, both within and at the end of the main chain [3]. Main outgassing fragments were seen at mass-to-charge ratios (m/z) equal to or below 20. The most dominant peak appeared at m/z = 20 assigned to hydrogen fluoride (HF), which was predicted as degradation product for the formation of unsaturations in the main chain [4]. Additional large signals were located at m/z = 2, 18, and 19 from hydrogen (H_2), residual water (H_2O), and fluorine (F), respectively. Other masses are assigned to CH_x fragments from the degradation of hydrocarbons. Importantly, dehydrofluorination occurs very efficiently to produce the C=C double bonds.

Therefore, we finally consider how the C=C double bonds could be oxidized efficiently. When the oxidant coexists, they are readily converted to C=O groups with a high water wettability enabling faster attack by the etchant. We chose ozone as the oxidant for the pre-etching treatment. PVDF films irradiated with 450-MeV ^{129}Xe ions were exposed to ozonized O_2 for 6 h at room temperature. Figure 1 shows our preliminary conductometry results. The conductance values on the ordinate are not converted to an effective pore diameter, d_{eff}, because the measurement was intended to analyze T_B for samples with and without the ozone treatment. The breakthrough time T_B of the ozone-treated film is about seven times shorter than that of the untreated film. This clearly demonstrates that the pre-etching treatment with a gaseous oxidant greatly accelerated the track etching rate. The reason for this effect is possibly linked to a quick reaction between ozone and alkenes to yield products in which the double bond is cleaved, such as ketones and carboxylic acids. It should be emphasized that this post-irradiation treatment method was achieved by the feedback from our findings regarding the basic chemistry in the track, quite in contrast to the previous study on ozone-induced track sensitization of PET films [5].

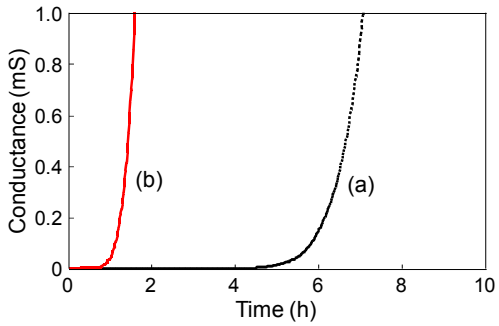

Fig. 1: Measured conductance vs. etching time for PVDF films irradiated with 450-MeV ^{129}Xe ions (a) with and (b) without treatment with ozone gas before the etching.

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